A NEW METHOD TO ESTIMATE HYDROGEN BONDINGS IN COAL BY UTILIZING FTIR AND DSC

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INTRODUCTION

Several attempts have been made to estimate the change in the macromolecular network of coal using DSC and F.T.i.r. techniques. Lucht et al.,[1] Mackinnon et al.,[2] and Yûn et al.[3] examined the glass transition of coal by the DSC measurement. Mackinnon et al.[2] observed the 2nd order phase glass transition at around 110 °C during the heating of various coals. They speculated that the 2nd order phase glass transition at low temperature was caused by the change in hydrogen bondings, although the direct evidence was not shown. We also demonstrated that a part of hydrogen bondings in coal are released between 100 and 200 °C from in-situ F.T.i.r. analysis.[4] Painter et al.[5] examined in detail the hydrogen bondings in coal using F.T.i.r., and classified the hydrogen bondings into 5 types.

In liquid phase, on the other hand, hydrogen-bonded adduct formation reactions between the OH functional groups of phenols and various bases have been examined in detail. The reaction is represented by

$$Ph\text{-}OH \;+\; B \;\longrightarrow\; Ph\text{-}OH\text{-}\text{-}B \qquad : \Delta H \qquad\qquad (1)$$
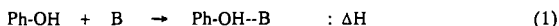
where Ph-OH--B represents the hydrogen-bonded adduct, and ΔH is the enthalpy change of the reaction. When the hydrogen bonding is formed, the wavenumber of the O-H stretching vibration shifts to a low wavenumber and generates heat ($\Delta H < 0$). The enthalpy change, ΔH, and the OH wavenumber shift, Δv_{OH}, were measured for various phenol-base combinations, and a linear relation was found to hold between ΔH and Δv_{OH} by many investigators.[6-9] The relation obtained by Drago et al.[6], for example, is given by

$$-\Delta H \;=\; 0.067\,\Delta v_{OH} \;+\; 2.64 \qquad \text{[kJ/mol]} \qquad\qquad (2)$$

The values of $-\Delta H$ was interpreted as the energy related to hydrogen bonding Ph-OH--B by many investigators.[10-13] However, Drago et al. thought that ΔH consists of two contributions: the change in the phenol O-H bond energy, δD_{OH}, and the bond dissociation energy of hydrogen bond formed, D_{HB}, as

$$\Delta H \;=\; \delta D_{OH} \;-\; D_{HB} \qquad\qquad (3)$$

They thought that D_{HB} is an index better than ΔH for the strength of the hydrogen bond. Then a relationship between δD_{OH} and Δv_{OH} as well as a relationship between D_{HB} and Δv_{OH} are required. They approximated the stretching of the hydrogen-bonded OH by the anharmonicity stretching of free OH, and related δD_{OH} with Δv_{OH} as follows:

$$\delta D_{OH} \;=\; (hcN/4\chi_e)\,\delta v_{OH} = D_{OHf}\,(\delta v_{OH}/v_e) = 0.131\Delta v_{OH} \qquad\qquad (4)$$

where h is Plank's constant, c is the speed of light, D_{OHf} is the bond dissociation energy of free O-H in kJ / mol and v_e is the wavenumber of harmonic vibration of the free OH in cm^{-1}, and χ_e is the anharmonicity constant for the oscillator.
From eqs.(2) and (4) D_{HB} was assumed to be represented by

$$D_{HB} \;=\; k\,\delta D_{OH} \;+\; \text{const.} \qquad\qquad (5)$$

Substituting eq.(4) into Eq.(5), the following equation is obtained.

$$D_{HB} \;=\; k_1\,\Delta v_{OH} \;+\; k_2 \qquad (k_1, k_2: \text{const.}) \qquad\qquad (6)$$

If the constants k_1 and k_2 can be determined, the relationship between D_{HB} and Δv_{OH} is obtained. In liquid phase the following equation has been established for the D_{HB}-Δv_{OH} relationship[6]:

$$-D_{HB} \;=\; 0.198\,\Delta v_{OH} \;+\; 2.64 \qquad \text{[kJ/mol]} \qquad\qquad (7)$$

In this paper an equation relating the bond dissociation energy of the hydrogen bonding, D_{HB}, and Δv_{OH} for coal was derived by extending the method of Drago et al. Then the strength distribution of hydrogen bondings in coal was estimated using the equation. Finally, the change in the hydrogen bondings through the heating of coal was examined.

EXPERIMENTAL

Sample preparation

A Japanese sub-bituminous coal, Taiheiyo (TC, C; 74.5%, H; 6.0%, N; 1.3%, S; 0.2%, O; 18.0% daf), was used as a raw coal. The coal was ground into fine particles of less than 74 μm, and dried in vacuo at 70 °C for 24 h before use. Irreversibly swollen coals (VDC) were prepared as follows: the coal particles were mixed with tetralin in a mass ratio of 1 to 0.6 in a stainless steel tube, and they were pressurized up to 1 MPa by nitrogen. The tube was immersed in a sand bath which was kept at a constant temperature at 150 or 220 °C and kept there for 1 h to prepare the swollen coal. Then, the swollen coal was evacuated at 70 °C for 24 h to remove completely the solvent retained. Even after removing the solvent the coal was still swollen to some extent. Then the coal was abbreviated to

VDC (vacuum dried coal). The VDCs prepared from the coals swollen at 150 and 220 °C were abbreviated to VDC(150°C) and VDC(220°C), respectively. The VDC(220°C) was further cooled to -100 °C using liquid nitrogen to prepare the sample in which some hydrogen bondings were restored. This sample was abbreviated to VDC(-100°C). The chars were prepared by pyrolyzing the coal at 5 K / min up to several temperatures to examine the change in hydrogen bondings during the pyrolysis.

F.T.i.r. and Calorimetric Measurement
The F.T.i.r. spectra of the raw coal, the VDCs and the pyrolysis chars were measured by the KBr method using a F.T.i.r. spectrometer (Shimadzu, FTIR 4300). The DSC profiles and the TG curves of the raw coal and the VDCs were measured under a constant heating rate of 5 K / min by use of a differential scanning calorimeter (Shimadzu, DSC 50) and a thermobalance (Shimadzu, TGA 50), respectively.

RESULTS AND DISCUSSION
Comparison of F.T.i.r. spectra between the raw coal and VDCs
The F.T.i.r. spectra were measured for all the samples. The spectrum of the O-H stretching vibration related to hydrogen bonding appears between 2600 and 3600 cm^{-1},[5] so the base line was drawn between these wavenumbers by a usual method.[14,15] Two sharp peaks at around 2800 cm^{-1} are due to aliphatic C-H vibrations, these peaks were eliminated following Solomon's method,[16] then the absorption peak related to hydrogen bondings was 3000 to 3600 cm^{-1} for TC coal. The spectra obtained after the treatment are shown by the dotted lines in Figure 1. Comparing the spectra, the intensity of peak at 3630 cm^{-1}, which is assigned as the free OH, is almost same for all the samples, indicating that free OH groups are not produced through the solvent swelling and the heat treatment. Many peaks are involved between 3000 and 3600cm^{-1} in the spectrum. Painter et al. showed that absorption bands of five hydrogen-bonded OH groups are involved in the spectrum: OH--π bonds (3516 cm^{-1}), self-associated OH groups (3400 cm^{-1}), OH--ether hydrogen bonds (3300 cm^{-1}), tightly bound cyclic hydrogen bonds (3200 cm^{-1}) and OH--N hydrogen bonds (2800-3100 cm^{-1}).[5] Following these assignments, each spectrum was fitted by five Lorentz-Gaussian distributions as shown by the solid lines in Fig.1. The OH wave number shift, Δv_{OHi}, for each hydrogen bonding is exactly estimated from the five peaks for the raw coal. The intensity of peak at around 3300 cm^{-1} was the strongest for the raw coal. As compared with the spectrum of the raw coal, the intensity of peak at around 3300 cm^{-1} decreased, and the intensities of peaks at around 3400 cm^{-1} and 3520cm^{-1} increased for VDC(220°C). The intensities of peaks at around 3400 cm^{-1} and 3520cm^{-1} decreased, and the intensity of peak at around 3300 cm^{-1} increased for VDC(-100°C). The intensities of peaks at around 3130 and 3040 cm^{-1} were almost same for all the samples. These results clearly show that the strong hydrogen bond and free OH were not affected by the solvent swelling and the heat treatment. Only the ether--OH, the self-associated OH groups, and the OH--π bonds were released or restored through the treatments.

Then we can visualize the change in the hydrogen bonding in coal as shown in Figure 2. When the coal is heated to as high as 200 °C or so, relatively weak hydrogen bonds such as OH--ether bond are released, but strong hydrogen bonds assigned at low wavenumber do not change. As a result the movement of the macromolecule of coal is restricted, then the OH in the hydrogen bonds released can not become free OH. It will form another weak hydrogen bonds.

Figure 3 shows the DSC profiles measured for the raw TC and the VDCs. Thermogravimetric (TG) curves were measured under the same conditions. Distinct differences were found among the DSC profiles at the temperature region of 100 to 300 °C, whereas no difference was found among the TG curves of the four samples. The DSC profile of the raw coal showed the largest endothermicity of the three samples: the endothermic rate started to increase at around 100 °C, reached a maximum at ca. 250 °C, decreased to reach a minimum at 300 °C or so, and finally increased rapidly with the further increase of temperature. On the other hand, the endothermic rate of VDC(220°C) whose swelling ratio was largest was almost constant up to 200 °C, then started to increase, and finally almost coincided with that of the raw coal. The endothermic rate of VDC(150°C) which was slightly swollen lay between the endothermic rates of the raw coal and VDC(220°C). The DSC profile of VDC(-100°C) was close to that of VDC(150°C) up to 200 °C, but over 200 °C it was closer to that of the raw coal. The difference between the DSC profiles of the raw coal and the VDCs is judged to arise from the differences in the hydrogen bondings among the samples. The difference of the enthalpy levels between the raw coal and the VDC at 25 °C, ΔH_C, is obtained by heating both samples up to 220 °C where both enthalpy levels are considered to be same as shown in Fig.4 The enthalpy ΔH_C could be related to the difference of the strength of hydrogen bondings between the samples.

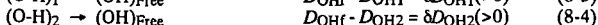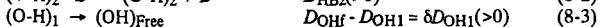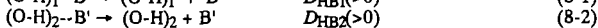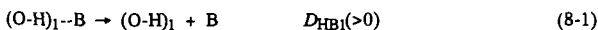### Estimation of the hydrogen bondings in coal using F.T.i.r. and DSC
a)Formulation of equation relating D_{HB} and Δv_{OH} in coal
The equation developed by Drago et al.[6] for relating D_{HB} and Δv_{OH} may not be applied to analyze the hydrogen bonding in coal, because it was obtained in liquid phase and coal contains several types of hydrogen bondings. However, the equation relating δD_{OH} and Δv_{OH}, eq.(4), was assumed to hold for the hydrogen-bonded OH in coal, because it is for intramolecule movement. Then the concept developed by Drago et al.[6] was extended to formulate the equation relating D_{HB} and Δv_{OH} using the experimental data, ΔH_C and Δv_i, obtained above.

First, we consider the change of a hydrogen bond, (O-H)$_1$--B, into another hydrogen bond, (O-H)$_2$--B', as a chemical reaction.

$$(O-H)_1\text{--}B + B' \rightarrow (O-H)_2\text{--}B' + B \qquad : \Delta H_C' \qquad (8)$$
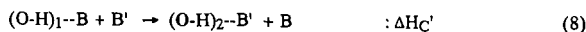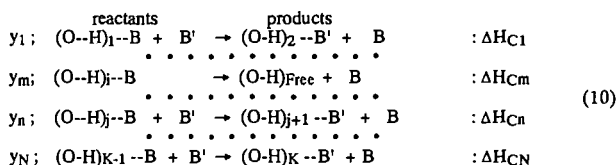
where B and B' represent electron donor atoms or molecules. The enthalpy change through the reaction, $\Delta H_C{}'$, is positive when the hydrogen bond becomes weaker through the reaction and *vice versa*. If we assume that $\Delta H_C{}' > 0$, the OH wavenumber shift decreases from Δv_{OH1} to Δv_{OH2}, and the O-H bond dissociation energy increases from D_{OH1} to D_{OH2} as shown in Fig.5. The above reaction was apparently divided into the following reactions:

$$
\begin{array}{lll}
(O-H)_1\text{--}B \rightarrow (O-H)_1 + B & D_{HB1}(>0) & (8\text{-}1) \\
(O-H)_2\text{-}B' \rightarrow (O-H)_2 + B' & D_{HB2}(>0) & (8\text{-}2) \\
(O-H)_1 \rightarrow (OH)_{Free} & D_{OHf} - D_{OH1} = \delta D_{OH1}(>0) & (8\text{-}3) \\
(O-H)_2 \rightarrow (OH)_{Free} & D_{OHf} - D_{OH2} = \delta D_{OH2}(>0) & (8\text{-}4)
\end{array}
$$

where $(O-H)_i$ represents the hydrogen-bonded OH groups, $(OH)_{Free}$ represents the free OH, D_{HBi} is the bond dissociation energy of hydrogen bond defined by Drago et al.,[6] and δD_{OHi} (i = 1, 2) is the difference of the dissociation energy of the free O-H bond, D_{OHf}, and that of hydrogen bonded O-H, D_{OHi}. Since eq.(8-1) - eq.(8-2) + eq.(8-3) - eq.(8-4) makes eq.(8), $\Delta H_C{}'$ is represented by

$$\Delta H_C{}' = (D_{HB1} - D_{HB2}) - (\delta D_{OH1} - \delta D_{OH2}) \qquad (9)$$

Next, eq.(8) was extended to all the reactions of the hydrogen bondings in coal as follows:

$$
\begin{array}{llll}
 & \text{reactants} & \text{products} & \\
y_1; & (O\text{--}H)_1\text{--}B + B' & \rightarrow (O\text{--}H)_2\text{--}B' + B & : \Delta H_{C1} \\
 & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\
y_m; & (O\text{--}H)_i\text{--}B & \rightarrow (O\text{--}H)_{Free} + B & : \Delta H_{Cm} \\
 & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & & (10) \\
y_n; & (O\text{--}H)_j\text{--}B + B' & \rightarrow (O\text{--}H)_{j+1}\text{--}B' + B & : \Delta H_{Cn} \\
 & \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot & \\
y_N; & (O\text{-}H)_{K-1}\text{--}B + B' \rightarrow (O\text{-}H)_K\text{--}B' + B & & : \Delta H_{CN}
\end{array}
$$

where all the possible reactions are taken into account in the N reactions, y_n is the contribution of each reaction defined so as to satisfy $\Sigma y_n = 1$, and the electron donors, B and B', for different reactions are not always same. The sum of $(O-H)_i$ and free OH, N_{OH} [mol/kg], is the total amount of OH groups in coal. The enthalpy change for each reaction, ΔH_{Cn}, is represented in the same manner as eq.(9). Then, summing up the reactions in eq.(10), the difference in the enthalpy between the products (p), and the reactants (r), ΔH_C [kJ/kg-coal], is represented by

$$
\begin{aligned}
\Delta H_C &= N_{OH} \Sigma y_n \Delta H_{Cn} \\
&= N_{OH} [\{\Sigma (\Sigma y_n)_i D_{HBi}\}_r - \{\Sigma (\Sigma y_n)_i D_{HBi}\}_p] \\
&\quad - N_{OH}[\{\Sigma (\Sigma y_n)_i \delta D_{OHi}\}_r - \{\Sigma (\Sigma y_n)_i \delta D_{OHi}\}_p] \qquad (11)
\end{aligned}
$$

where y_n is set equal to 0 when i-th species is not involved in the n-th reaction. Then the term $(\Sigma y_n)_i$ is equal to the fraction of hydrogen-bonded $(O-H)_i$ of the all OH, and it was represented by f_i. The terms $\Sigma (\Sigma y_n)_i D_{HBi}$ and $\Sigma (\Sigma y_n)_i \delta D_{OHi}$, therefore, correspond to the average values of D_{HB} and δD_{OH}, respectively. They were represented by $\overline{D}_{HB}$ and $\overline{\delta D}_{OH}$, respectively. By using the representation eq.(9) is rewritten as

$$(\overline{D}_{HB})_r - (\overline{D}_{HB})_p = \Delta H_C / N_{OH} + [(\overline{\delta D}_{OH})_r - (\overline{\delta D}_{OH})_p] \qquad (12)$$

By inserting eqs.(4) and (6) into δD_{OHi} and D_{HBi} in eq.(11), eq.(13) is rewritten as

$$k_1\{(\Delta \overline{v}_{OH})_r - (\Delta \overline{v}_{OH})_p\} = \Delta H_C / N_{OH} + 0.131\{(\Delta \overline{v}_{OH})_r - (\Delta \overline{v}_{OH})_p\} \qquad (13)$$

where

$$\Delta \overline{v}_{OH} = \Sigma (\Sigma y_n)_i \Delta v_{OHi} = \Sigma f_i \Delta v_{OHi} \qquad (14)$$

Thus a general equation relating ΔH_C and Δv_{OHi} was formulated. When the raw coal and one of the VDCs are chosen as the reactants and the products in eq.(13), respectively, ΔH_C was measured by DSC, and Δv_{OHi} (i = 1 ~ 5) were measured by F.T.i.r. for both the raw coal and the VDC as stated above. The value of N_{OH} could be determined from ^{13}C-n.m.r. Then, knowing f_i, the k_1 value in eq.(13) can be determined. The value of f_i can be determined from the F.T.i.r. spectra if the relative sensitivities of the five peaks are known. Since the sensitivities are not known now, they were assumed to be same as a first approximation. Then the relations between D_{HB}, ΔH and Δv_{OH} could be obtained as

$$D_{HB} = 0.20 \Delta v_{OH} \qquad (15)$$
$$\Delta H = 0.069 \Delta v_{OH} \qquad (16)$$

Figure 6 compares the D_{HB}-Δv_{OH} and ΔH-Δv_{OH} relationships obtained here (eqs.(15) and (16)) with those obtained by Drago et al. in liquid phase (eqs.(7) and (2)). The experimental data in liquid phase obtained by several researchers[6-9] are also shown. Eqs.(16) and (2) were very close, and they correlate the experimental data very well. Eqs.(15) and (7) also almost coincided. This shows that same D_{HB}-Δv_{OH} and ΔH_{HB}-Δv_{OH} relationships hold in liquid phase and solid phase, and that eq.(15) is valid to estimate the hydrogen bondings in coal.

(b)Estimation of the strength distribution of hydrogen bonding in coal
Once eq.(15) is found to be valid, the strength distribution of hydrogen bond in coal is straightforwardly estimated. The hydrogen bondings in coal were represented by 5 types, and they were approximated by Gauss-Lorentz functions as stated earlier. The amount of OH corresponding

to each hydrogen bonding, n [mol/mol], is calculated from the intensity of each peak, and D_{HB} corresponding to the peak is calculated from Δv_{OHi} using eq.(15). Then, plotting the n values against D_{HBi}, we can obtain the strength distribution of hydrogen bonding. The values of D_{OHi} and δD_{OHi} are also obtained using eqs.(3), (15) and (16).

Figure 7 shows the strength distributions of hydrogen bondings in the raw TC coal and the VDCs. The values of D_{HB}, D_{OH}, and ΔH at maximum n value were 68.0, 42.0 and 23.8 kJ/mol-OH, respectively, for the raw coal. The value of 23.8 kJ/mol-OH for ΔH is reasonable, judging from the values reported.[10-13] The strength distribution for VDC(220°C) shows that the hydrogen bondings of D_{HB} = 68.0 and 90.0 kJ/mol-OH decreased, but the hydrogen bondings of D_{HB} = 22.8 and 42.0 kJ/mol-OH increased through swelling.

(c)Change in the strength distribution of hydrogen bonding during the pyrolysis
The change in the strength distribution of hydrogen bonding during the pyrolysis was examined by applying eq.(16) to the pyrolysis chars prepared at several pyrolysis temperatures as shown in Fig.8. When TC coal was heated to 280 °C, the 2nd phase glass transition temperature, the hydrogen bonding of D_{HB} = 68 to 90 kJ/mol-OH decreased, and the hydrogen bonding of D_{HB} = 42 kJ/mol-OH increased, indicating that the macromolecular network of the coal was altered to a loose network. The strong hydrogen bondings of D_{HB} = 90 kJ/mol-OH was disappeared first when the coal was heated from 386 to 485 °C, then the weak hydrogen bondings disappeared at around 500 °C. These results indicate that the stronger hydrogen bonding sites become the crosslinking site at low temperature. This well coincides with the fact that the value of D_{OH} decreases as the hydrogen bonding becomes stronger.

Thus, the presented equation was found to be very useful for estimating directly the hydrogen bonding in coal. We have made several assumptions and approximations to derive the equation. We will examine the validity of the assumptions and the approximations in future works.

CONCLUSION
A new method was presented for estimating the strength distribution of hydrogen bonding in coal by use of F.T.i.r. and DSC. An equation relating the dissociation energy of hydrogen bonding, D_{HB}, with the OH wavenumber shift, Δv_{OH}, was established by utilizing the change of hydrogen bonding between a Taiheiyo coal and irreversibly swollen coal prepared from the coal. Using the equation, we could estimate the strength distribution of hydrogen bonding in the coal. The peak D_{HB} value of the raw coal was found to be about 68 kJ/mol-OH. The change in the hydrogen bondings through the pyrolysis of coal was well represented by the method.

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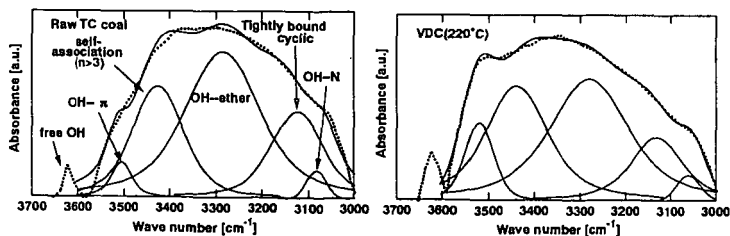16.Solomon, P.R.; Carangelo, R.M., *Fuel,*1988, 67, 949-959.

Figure 1 Comparison of the OH stretching vibration between the raw TC and a swollen coal.
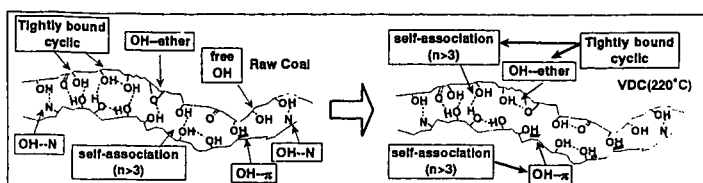
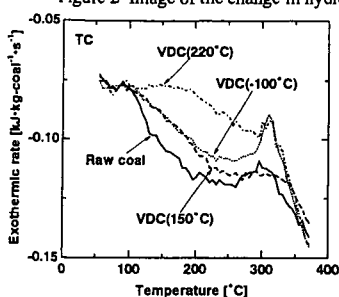Figure 2 Image of the change in hydrogen bondings in coal through the treatment.

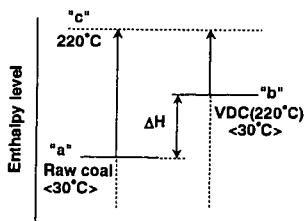Figure 3 DSC profiles of the raw TC
and the VDCs.

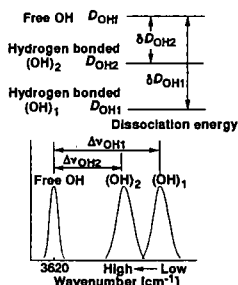Figure 4 Enthalpy levels of the raw
TC and VDC(220°C).

Figure 5 Changes in OH bond energy, D_{OH}, and
wavenumber shift, Δv_{OH}, accompanied
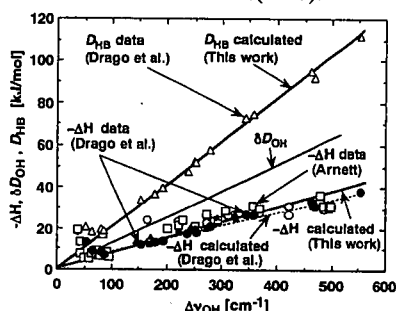the change of a hydrogen bonding in coal.

Figure 6 Comparison of the values of D_{HB}
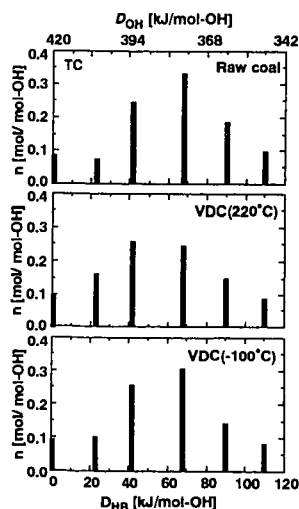and ΔH calculated by eqs.(15), (16)
with the experimental data.

Figure 7 Strength distributions of hydrogen
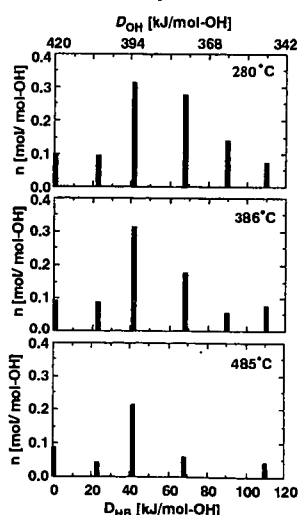bondings in TC coal and the VDCs.

Figure 8 Change in strength distributions of
hydrogen bondings in TC coal
through the heat treatment.

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